(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 September 2003 (25.09.2003)

PCT

(10) International Publication Number
WO 03/078513 A1

(51) International Patent Classification⁷: C08J 7/04, B41M 5/00, C09D 133/06

(21) International Application Number: PCT/GB03/00976

(22) International Filing Date: 5 March 2003 (05.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0205800.6 12 March 2002 (12.03.2002) GB

(71) Applicant *(for all designated States except US)*: **DUPONT TEIJIN FILMS U.S. LIMITED PARTNERSHIP** [US/US]; Building 27, Barley Mill Plaza, Routes 141 & 48, Wilmington, DE 19805 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **LOGAN, Moira** [GB/GB]; 18 Fairville Road, Stockton-on-Tees TS19 7NA (GB). **PANKRATZ, Richard, Paul** [US/US]; 167 Brookhill Lane, Circleville, OH 43113 (US). **FUKUDA, Masayuki** [JP/JP]; 1357 Minamijo, Anpachi-cho, Anpachi-gun, Gifu 503-0123 (JP). **BRABBS, Noel, Stephen** [GB/LU]; 29, rue des Trois Cantons, L-8354 Garnich (LU).

(74) Agent: **COCKERTON, Bruce, Roger**; Carpmaels & Ransford, 43 Bloomsbury Square, London WC1A 2RA (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 03/078513 A1

(54) Title: COATED POLYMERIC FILM SUBSTRATES FOR RADIATION-CURABLE INK

(57) Abstract: Use of a primer layer and a secondary layer as a coating on a polymeric substrate, wherein the primer layer is in contact with the substrate layer and the secondary coating layer is in contact with the primer layer, wherein said secondary layer comprises an acrylic resin, and wherein said secondary layer is not cross-linked or comprises less than 5 % by weight of a cross-linking agent based on the weight of the acrylic resin in the secondary coating composition, for the purpose of improving adhesion of radiation-curable ink to said substrate in a printing process comprising a plurality of radiation-curing steps; and a polymeric substrate coated with said coating wherein the secondary layer is not cross-linked or has a low degree of cross-linking.

COATED POLYMERIC FILM SUBSTRATES FOR RADIATION-CURABLE INK

The present application is concerned with coated polymeric films suitable as substrates for inks curable by radiation, particularly by ultraviolet radiation.

Polymeric films have been used in a variety of applications, including magnetic tape, photographic film, display film and protective film. Polyester films, particularly biaxially oriented films of poly(ethylene terephthalate), are particularly useful since they have good mechanical properties, heat resistance and chemical resistance. The polyester film is, in many instances, used in association with a second layer, for instance a magnetic layer, a photosensitive layer or a hard protective layer. Accordingly, the polyester film must have good adhesion to the subsequently applied layer and for this purpose the polyester substrate is often provided with a primer layer.

For instance, JP-A-61/85436 discloses a polyester substrate onto which is coated an aqueous dispersion of a polyester comprising terephthalic acid at 40-95 mol% and 5-sodiumsulphoisophthalic acid (5-SIPA) at 0.5-5 mol% of the total acid component; and ethylene glycol and an etherglycol, wherein the etherglycol comprises 5-70 mol% of the total glycol component. The primer coating is described as providing good adhesion to magnetic coatings as well as good blocking resistance (windability).

Polyester films have also been used as substrates for printed information, images and other graphic work. In these applications, the polyester film usually has an ink-adherable or primer layer applied thereto. In certain applications, the ink used in the printing is a radiation-curable ink, for instance by ultraviolet radiation or by electron-beam. The use of radiation-curable inks offers advantages since they are generally faster to process, and do not require drying since they contain no solvents. The absence of solvent also means that fewer volatile organic compounds are released in comparison with thermally-cured inks. For applications requiring multi-colour printing, or layering of multiple images, several separate printing steps may be required. After each printing step, the printed film is cured with radiation. Thus, the final printed multi-colour film has undergone multiple printing steps and multiple radiation-curing steps.

However, a problem with known films is that the adhesive power of the primer layer to anchor a radiation-curable ink to the substrate deteriorates with multiple radiation curing steps, especially when UV radiation is used to cure the ink. While the adhesion of a radiation-cured ink applied to the primed substrate in a first printing curing step is not necessarily adversely affected by subsequent printing and curing steps, the adhesive power of the primed substrate to subsequently applied radiation-cured inks will progressively deteriorate with each subsequent printing and curing cycle. Thus, when several different curable inks are printed and cured to produce an image, the primed film exhibits progressively poorer adhesion to subsequently applied inks as the number of curing steps increases.

Polycarbonate films have previously been used as printable substrates suitable for radiation-curable inks requiring multiple radiation curing steps. However, such films are generally more expensive than polyester substrates, and have poorer resistance to heat, organic solvents and other environmental damage. It would be desirable to provide a more durable and lower cost alternative to polycarbonate films.

It is an object of this invention to provide a film suitable as a substrate for radiation-curable inks, particularly UV-curable inks, which demonstrates improved adhesion after multiple radiation-curing steps. It is a further object of this invention to provide a more durable and lower cost substrate for radiation-curable inks, particularly UV-curable inks, which demonstrates improved adhesion after multiple radiation-curing steps.

According to the present invention, there is provided the use of a first layer, hereinafter referred to as the primer layer, and a second layer, hereinafter referred to as the secondary layer, as a coating on a polymeric substrate, wherein the primer layer is in contact with the substrate layer and the secondary coating is in contact with the primer layer, wherein said secondary layer comprises an acrylic resin, and wherein said secondary layer is not cross-linked or comprises less than 5% by weight of a cross-linking agent based on the weight of the acrylic resin in the secondary coating composition, for the purpose of improving adhesion of radiation-curable ink to said substrate in a printing process comprising a plurality of radiation-curing steps.

According to a further aspect of the present invention, there is provided a method of improving the adhesion of radiation-curable ink to a polymeric substrate in a printing process comprising a plurality of radiation-curing steps, said method comprising the application of a primer layer to a surface of said substrate and said method further comprising the application of a secondary layer comprising an acrylic resin to a primed surface of said primed substrate and wherein said secondary layer is not cross-linked or comprises less than 5% by weight of a cross-linking agent based on the weight of the acrylic resin in the secondary coating composition. The method of the invention optionally further comprises applying one or more radiation-curable ink(s) according to a process known in the art, and curing the ink(s) in one or more radiation-curing step(s).

The use and method described above are particularly useful wherein a plurality of radiation-curable inks and a plurality of curing steps are used to generate an image or design from said radiation-curable inks, particularly wherein said radiation is UV radiation.

The inventors have unexpectedly found that the use of the coating layers described herein provides an adhesive force to subsequently applied radiation-curable inks which is relatively resistant to repeated exposure to radiation, particularly UV radiation, such that the adhesion of radiation-curable inks to the substrate does not diminish on successive curing steps.

Furthermore, the inventors have unexpectedly found that adhesion of the coated substrate to radiation-curable inks is increased when the secondary layer is not cross-linked or has a low degree of cross-linking. A secondary layer which has a low degree of cross-linking comprises less than 5 % by weight, preferably less than 2% by weight, more preferably less than 1% by weight, and most preferably less than 0.5% by weight of a cross-linking agent, based on the weight of the acrylic resin in the secondary layer. An absence or a low degree of cross-linking is believed to increase the resistance of the polymeric layer to degradation by the radiation used in the curing of the inks. It is not, however, intended that the invention be limited by this theory.

According to a further aspect of the invention, there is provided a polymeric film comprising a polymeric substrate having on at least one surface thereof a coating

comprising a primer layer and a secondary layer, wherein the primer layer is in contact with the substrate layer and the secondary coating layer is in contact with the primer layer, wherein said secondary layer comprises an acrylic resin, and wherein the secondary layer is not cross-linked or comprises less than 1% by weight, preferably less than 0.5% by weight, of a cross-linking agent.

The polymeric film is particularly suitable as a substrate for an image consisting of a plurality of radiation-cured inks, and which requires a plurality of radiation curing steps, particularly wherein said radiation is UV radiation. Such an image may require at least 2, 3 or 4 curing steps and often as many as 10 or more curing steps.

Typically, radiation-curable inks comprise a mixture of monomer(s), oligomer(s), photoinitiator(s) and pigment(s). The present invention is of particular use for radiation-curable inks wherein the oligomer(s) comprise an acrylate resin and/or silicones, particularly acrylate resins selected from the group consisting of acrylic resins, urethane-acrylate resins, epoxy-acrylate resins and polyester-acrylate resins. The monomeric component(s) typically include acrylate monomer(s) and/or acrylated polyols or polyamines having mono-, bi- or tri-functionality. In addition, such inks generally have a low to medium degree of internal cross-linking (typically up to about 25% by weight of a cross-linking agent), and contain pigments, dyes or other colourants. The invention is advantageous in that it improves the adhesion between the substrate and the radiation-curable ink requiring multiple radiation curing steps, as is necessary when several inks are printed and cured sequentially to build up the desired image or graphic, such as in the production of coloured images.

The polymeric substrate layer is a self-supporting film or sheet by which is meant a film or sheet capable of independent existence in the absence of a supporting base. The substrate may be formed from any suitable film-forming polymer, preferably polyester, and particularly a synthetic linear polyester.

The synthetic linear polyesters useful as the substrate may be obtained by condensing one or more dicarboxylic acids or their lower alkyl (up to 6 carbon atoms) diesters, eg terephthalic acid, isophthalic acid, phthalic acid, 2,5-, 2,6- or 2,7-naphthalenedicarboxylic

acid, succinic acid, sebacic acid, adipic acid, azelaic acid, 4,4'-diphenyldicarboxylic acid, hexahydro-terephthalic acid or 1,2-bis-p-carboxyphenoxyethane (optionally with a monocarboxylic acid, such as pivalic acid) with one or more glycols, particularly an aliphatic or cycloaliphatic glycol, e.g. ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol and 1,4-cyclohexanedimethanol. An aromatic dicarboxylic acid is preferred. An aliphatic glycol is preferred. Polyesters or copolyesters containing units derived from hydroxycarboxylic acid monomers, such as ω-hydroxyalkanoic acids (typically $C_3$-$C_{12}$) hydroxypropionic acid, hydroxybutyric acid, p-hydroxybenzoic acid, m-hydroxybenzoic acid or 2-hydroxynaphthalene-6-carboxylic acid, may also be used.

In a preferred embodiment, the polyester is selected from polyethylene terephthalate and polyethylene naphthalate. Polyethylene terephthalate (PET) is particularly preferred.

The substrate may comprise one or more discrete layers of the above film-forming materials. The polymeric materials of the respective layers may be the same or different. For instance, the substrate may comprise one, two, three, four or five or more layers and typical multi-layer structures may be of the AB, ABA, ABC, ABAB, ABABA or ABCBA type. Preferably, the substrate comprises only one layer.

Formation of the substrate may be effected by conventional techniques well-known in the art. Conveniently, formation of the substrate is effected by extrusion, in accordance with the procedure described below. In general terms the process comprises the steps of extruding a layer of molten polymer, quenching the extrudate and orienting the quenched extrudate in at least one direction.

The substrate may be uniaxially-oriented, but is preferably biaxially-oriented, as noted above. Orientation may be effected by any process known in the art for producing an oriented film, for example a tubular or flat film process. Biaxial orientation is effected by drawing in two mutually perpendicular directions in the plane of the film to achieve a satisfactory combination of mechanical and physical properties.

In a tubular process, simultaneous biaxial orientation may be effected by extruding a thermoplastics polymer tube which is subsequently quenched, reheated and then expanded

by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation.

In the preferred flat film process, the substrate-forming polymer is extruded through a slot die and rapidly quenched upon a chilled casting drum to ensure that the polymer is quenched to the amorphous state. Orientation is then effected by stretching the quenched extrudate in at least one direction at a temperature above the glass transition temperature of the polyester. Sequential orientation may be effected by stretching a flat, quenched extrudate firstly in one direction, usually the longitudinal direction, i.e. the forward direction through the film stretching machine, and then in the transverse direction. Forward stretching of the extrudate is conveniently effected over a set of rotating rolls or between two pairs of nip rolls, transverse stretching then being effected in a stenter apparatus. Alternatively, the cast film may be stretched simultaneously in both the forward and transverse directions in a biaxial stenter. Stretching is effected to an extent determined by the nature of the polymer, for example polyethylene terephthalate is usually stretched so that the dimension of the oriented film is from 2 to 5, more preferably 2.5 to 4.5 times its original dimension in the or each direction of stretching. Typically, stretching is effected at temperatures in the range of 70 to 125°C. Greater draw ratios (for example, up to about 8 times) may be used if orientation in only one direction is required. It is not necessary to stretch equally in the machine and transverse directions although this is preferred if balanced properties are desired.

A stretched film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint at a temperature above the glass transition temperature of the polyester but below the melting temperature thereof, to induce crystallisation of the polyester. The actual heat-set temperature and time will vary depending on the composition of the film but should not be selected so as to substantially degrade the mechanical properties of the film. Within these constraints, a heat set temperature of about 135° to 250°C is generally desirable, as described in GB-A-838708.

The film may be further heat-stabilised by heating it under low tension (i.e. with the minimum possible dimensional restraint) at a temperature above the glass transition temperature of the polyester but below the melting point thereof, in order to allow the

majority of the inherent shrinkage in the film to occur (relax out) and thereby produce a film with very low residual shrinkage and consequently high dimensional stability. The tension experienced by the film during this heat-stabilisation step is typically less than 5 kg/m, preferably less than 3.5 kg/m, more preferably in the range of from 1 to about 2.5 kg/m, and typically in the range of 1.5 to 2 kg/m of film width. The temperature to be used for the heat stabilisation step can vary depending on the desired combination of properties from the final film, with a higher temperature giving better, i.e. lower, residual shrinkage properties. The duration of heating will depend on the temperature used but is typically in the range of 10 to 40 sec, with a duration of 20 to 30 secs being preferred. This heat stabilisation process can be carried out by a variety of methods, including flat and vertical configurations and either "off-line" as a separate process step or "in-line" as a continuation of the film manufacturing process.

Where the substrate comprises more than one layer, preparation of the substrate is conveniently effected by coextrusion, either by simultaneous coextrusion of the respective film-forming layers through independent orifices of a multi-orifice die, and thereafter uniting the still molten layers, or, preferably, by single-channel coextrusion in which molten streams of the respective polymers are first united within a channel leading to a die manifold, and thereafter extruded together from the die orifice under conditions of streamline flow without intermixing thereby to produce a multi-layer polymeric film, which may be oriented and heat-set as hereinbefore described. Formation of a multi-layer substrate may also be effected by conventional lamination techniques, for example by laminating together a preformed first layer and a preformed second layer, or by casting, for example, the first layer onto a preformed second layer.

The substrate layer is suitably of a thickness between about 5 and 350μm, preferably from 50 to about 300 μm and particularly from about 75 to about 250μm.

The primary function of the primer layer is to improve adhesion and delamination resistance between the polymeric substrate and the acrylic secondary layer. The system has improved resistance to degradation by radiation, particularly UV radiation, experienced in subsequent radiation curing steps of radiation-curable inks.

The primer layer should therefore comprise a polymer which is compatible with the substrate and the acrylic resin-containing secondary layer, by which is meant a polymer which exhibits good adhesion (in particular good monomer-resistant adhesion) to both the substrate and to the acrylic resin of the secondary layer.

In one embodiment, the primer layer comprises a polymer which is capable of improving the adhesion, and in particular the monomer-resistant adhesion, between a polyester substrate, particularly a polyethylene terephthalate substrate, and an acrylic resin-containing layer. Any polymer suitable for this purpose may be used, including polyesters, polyurethanes, acrylics, vinylidene chloride-based polymers, polyvinylacetates and the like. Such polymers may be used in the primer layer either alone or as a polymer blend, and may be cross-linked or not cross-linked.

In a preferred embodiment, the primer layer composition is selected from the group consisting of:
(i) a composition comprising an aqueous polyester having a glass transition point (Tg) of 20 to 85°C, preferably 30 to 85°C, preferably from 35 to 80°C; and
(ii) an acrylic and/or methacrylic polymeric resin.

In one embodiment, the aqueous polyester has a Tg of from 40 to 85°C, and particularly from 45 to 80°C.

The aqueous polyester is a water-soluble or water-dispersible polyester. The aqueous polyester is a polyester produced from a polycarboxylic acid component such as terephthalic acid, isophthalic acid, phthalic acid, 2,6-naphthalenedicarboxylic acid, hexahydroterephthalic acid, 4,4'-diphenyldicarboxylic acid, phenylindanedicarboxylic acid, adipic acid, sebacic acid, sodium 5-sulfoisophthalic acid (5-SIPA), potassium 5-sulfoisophthalic acid, trimellitic acid or the like and a polyhydroxy compound component such as ethylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, glycerine, trimethylolpropane or an addition product of bisphenol A with an alkylene oxide (particularly ethylene oxide). In one embodiment, the aqueous polyester comprises a polyether component. In a further

embodiment, the aqueous polyester comprises a component containing an $SO_3^-$ group (particularly an $SO_3Na$ group) or a $COO^-$ group (particularly a COONa group).

In a preferred embodiment, the aqueous polyester is a water-dispersible polyester hereinafter referred to as AP1 wherein the polycarboxylic acid component of the aqueous polyester comprises terephthalic acid at 40-99.5 mol% and 5-sodiumsulphoisophthalic acid (5-SIPA) at 0.5-5 mol% of the total acid component; and the polyhydroxy component of the aqueous polyester comprises ethylene glycol and an etherglycol, wherein the etherglycol comprises 5-70 mol%of the total glycol component, and wherein the etherglycol has formula (I),

$$H(OC_nH_{2n})_m\text{-}O\text{-}A\text{-}O\text{-}(C_nH_{2n}O)_lH \qquad (I)$$

wherein

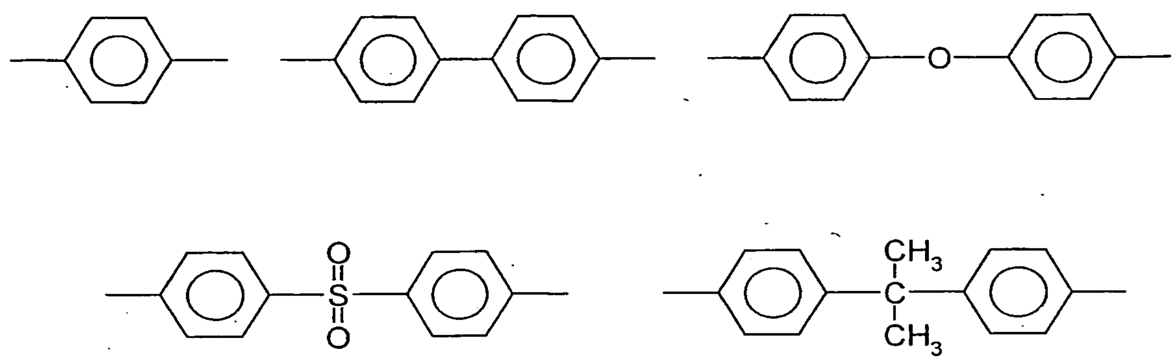
A is a bivalent aromatic hydrocarbon having 6 - 20 carbon atoms;

n is an integer 2 – 4; and

l and m, which can be the same or different, are 0, 1 or higher wherein $2 \leq (m+l) \leq 10$.

In the embodiment of the invention wherein the primer composition comprises aqueous polyester AP1, the content of terephthalic acid in the aqueous polyester is preferably greater than 60 mol%, more preferably greater than 80 mol% and most preferably greater than 85 mol%. Preferably, the content of the 5-SIPA component in the aqueous polyester is 1 to 5 mol% and more preferably 1 to 3 mol%. The aqueous polyester contains terephthalic acid and 5-SIPA in the stated ranges but can also contain other polycarboxylic acids such as those mentioned above, including aromatic dicarboxylic acids such as isophthalic acid, phthalic acid and diphenyldicarboxylic acid, and/or aliphatic dicarboxylic acids such as adipic acid, azeleic acid and sebacic acid, and/or alicyclic dicarboxylic acids such as 1,3-cyclohexanedicarboxylic acid and 1,4- cyclohexanedicarboxylic acid. Of these, aromatic dicarboxylic acids are preferred, preferably isophthalic acid. The other dicarboxylic acids are preferably present at levels of no more than 50 mol%, preferably, no more than 30 mol%, preferably no more than 15 mol% and preferably no more than 10 mol% of the total acid component of the aqueous polyester.

In the embodiment of the invention wherein the primer composition comprises aqueous polyester AP1, the preferred content of the etherglycol is 10 - 60 mol%. The group A in the etherglycol of formula (I) is preferably selected from [1,4-phenyl], [4,4'-biphenyl], [4,4'-diphenylether], [4,4'-diphenylsulphone] and a [bisphenol A] residue, preferably a [bisphenol A] residue. Thus, A is preferably selected from:



In the etherglycols of formula (I), it is preferred that n = 2 and that $2 \leq (m+l) \leq 8$. The ethylene glycol component may be replaced by up to 20 mol% or up to 10 mol% by other aliphatic glycols such as the glycols mentioned above, including 1,4-butanediol and 1,4-cyclohexanedimethanol.

In the embodiment of the invention wherein the primer composition comprises aqueous polyester AP1, the IV of the copolyester is preferably 0.2 - 0.8. The copolyester AP1 is essentially insoluble in water, meaning that if 3-5 mm chips are placed in hot water at 90°C for 3 hours, the weight loss is less than 1 wt%, preferably less than 0.5wt% and most preferably less than 0.1 wt%.

Suitable aqueous polyesters for use in the present invention include:

(a) a copolyester comprising terephthalic acid (90 mol %), isophthalic acid (6 mol %), potassium 5-sulfoisophthalate (4 mol %), ethylene glycol (95 mol %) and neopentyl glycol (5 mol %) (Tg=68°C);

(b) a copolyester comprising 2,6-naphthalenedicarboxylic acid (50 mol %), terephthalic acid (46 mol %), sodium 5-sulfoisophthalate (4 mol %), ethylene glycol (70 mol %), and addition product of bisphenol A with ethylene oxide (30 mol %) (Tg=80°C);

(c) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (15 mol %), ethylene glycol (57 mol %), 1,4-butanediol (40 mol %), diethylene glycol (2 mol %), and polyethylene glycol (1 mol %) (Tg=47°C);

(d) a copolyester comprising terephthalic acid (70 mol %), isophthalic acid (28 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (30 mol %) (Tg=30°C);

(e) a copolyester comprising 2,6-naphthalenedicarboxylic acid (71 mol %), isophthalic acid (15 mol %), sodium 5-sulfoisophthalate (14 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 2 molar ethylene oxide (30 mol %) (Tg=90°C);

(f) a copolyester comprising terephthalic acid (50 mol %), isophthalic acid (48 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (50 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (50 mol %) (IV = 0.55);

(g) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (13 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (50 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (50 mol %) (IV = 0.61);

(h) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (13 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (30 mol %) (IV = 0.65); and

(i) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (11 mol %), sodium 5-sulfoisophthalate (4 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (30 mol %) (IV = 0.58).

(j) a copolyester comprising terephthalic acid (97 mol %), isophthalic acid (1 mol %), sodium 5-sulphoisophthalate (2 mol %), ethylene glycol (60 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (40 mol %) (IV = 0.58);

(k) a copolyester comprising naphthalene dicarboxylic acid (60 mol %), isophthalic acid (36 mol %), sodium 5-sulphoisophthalic acid (4 mol %), ethylene glycol (60 mol %), and addition product of 1 mole bisphenol A with 2 moles propylene oxide (40 mol %).

The values of mol% for the components of the copolyesters (a) to (k) above represent the relative proportions of that component in terms of the total acidic component, or in terms of the total glycol component, as appropriate.

The preparation and further exemplification of suitable aqueous polyesters are disclosed in JP-A-61/85436 and US-5910356, the disclosures of which are incorporated herein by reference.

In the embodiments wherein the primer layer comprises an acrylic and/or methacrylic polymeric resin, suitable polymers comprise at least one monomer derived from an ester of acrylic acid, preferably an alkyl ester wherein the alkyl group is a $C_{1-10}$ alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, hexyl, 2-ethylhexyl, heptyl and n-octyl, and more preferably ethyl and butyl. Polymers comprising alkyl acrylate monomer units and further comprising alkyl methacrylate monomer units are particularly preferred. In a particularly preferred embodiment, the polymer comprises ethyl acrylate and alkyl methacrylate. Preferably, the alkyl methacrylate is methyl methacrylate. In a preferred embodiment, the alkyl acrylate monomer units are present in a proportion in the range of from about 30 to about 65 mole % and the alkyl methacrylate monomer units are present in a proportion in the range of from about 20 to about 60 mole %.

Other monomer units which may be present in the acrylic/methacrylic polymeric resin of the primer layer include acrylonitrile, methacrylonitrile, halo-substituted acrylonitrile, halo-substituted methacrylonitrile, acrylamide, methacrylamide, N-methylol acrylamide, N-ethanol acrylamide, N-propanol acrylamide, N-methacrylamide, N-ethanol methacrylamide, N-methylacrylamide, N-tertiary butyl acrylamide, hydroxyethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, dimethylamino ethyl methacrylate, itaconic acid, itoconic anhydride and half ester of itaconic acid.

Further monomer units which may be present in the acrylic/methacrylic polymeric resin of the primer layer include vinyl esters such as vinyl acetate, vinyl chloracetate and vinyl benzoate, vinyl pyridine, vinyl chloride, vinylidene chloride, maleic acid, maleic anhydride, styrene and derivatives of styrene such as chlorostyrene, hydroxystyrene and alkylated styrenes wherein the alkyl group is a $C_{1-10}$ alkyl group.

In a preferred embodiment, the acrylic/methacrylic polymeric resin of the primer layer comprises ethyl acrylate, methyl methacrylate and methacrylamide, particularly wherein

the polymeric resin comprises about 35 to 60 mole % ethyl acrylate, about 30 to 55 mole % methyl methacrylate and about 2 to 20 mole % methacrylamide.

In a further preferred embodiment, the primer layer comprises a copolymer of vinylidene chloride, methyl acrylate, ethyl acrylate and itaconic acid, particularly wherein the vinylidene chloride is present in a proportion in the range of from 60 to 70 mole %, the methyl acrylate is present in a proportion in the range of from 5 to 10 mole %, the ethyl acrylate is present in a proportion in the range of from 20 to 30 mole % and the itaconic acid is present in a proportion in the range of from 0.5 to 2 mole %

Preferably, the molecular weight of the acrylic/methacrylic polymeric resin of the primer layer is from about 40,000 to about 300,000, and more preferably from about 50,000 to about 200,000.

In the embodiments wherein the primer layer comprises an acrylic/methacrylic polymeric resin, the layer optionally further comprises a cross-linking agent which improves adhesion to the substrate and to the subsequently applied secondary layer. The cross-linking agent should also be capable of internal cross-linking within the primer layer composition. A cross-linking agent may be in the form of a reactive monomer or monomers co-polymerised in the polymer chain of the acrylic resin, and/or in the form of a separate species capable of reacting with active sites on the acrylic chains. Suitable cross-linking agents include epoxy-resins, alkyd resins, oxazolidines, polyfunctional aziridines, resorcinol, phenolformaldehyde resins, amine derivatives (such as hexamethoxymethylmelamine) and condensation products of an amine (such as melamine, diazine, urea, cyclic ethylene urea, cyclic propylene urea, thiourea, cyclic ethylene thiourea, alkyl melamines, aryl melamines, benzo guanamines, guanamines, alkyl guanamines and aryl guanamines) with an aldehyde, for example formaldehyde. Preferred cross-linking agents include polyfunctional aziridines. A further preferred cross-linking agent is a condensation product of melamine with formaldehyde, optionally alkoxylated, for example methoxylated or ethoxylated. The primer layer comprising an acrylic/methacrylic polymeric resin may include a cross-linking catalyst, such as ammonium chloride, ammonium nitrate, ammonium thiocyanate, ammonium dihydrogen phosphate, ammonium sulphate, diammonium hydrogen phosphate, para-toluene sulphonic

acid, and morpholinium para-toluene sulphonate. The cross-linking agent is preferably used in amounts of up to about 25% by weight based on the weight of the polymer in the coating composition.

In the embodiment where the primer layer is a polyurethane, suitable polymers are disclosed in, for example, US-5667889 and US-5910370, the disclosures of which are incorporated herein by reference.

The primer coating layer is preferably applied in the form of a composition in which the polymer component described above is present in an amount of 0.3 to 20% by weight, preferably 2 to 8% by weight, based on the total weight of the coating composition. The primer layer may be applied to one or both surfaces of the substrate.

The primer coating composition may be applied to an already oriented substrate. However, application of the primer coating composition is preferably effected before or during the stretching operation(s). For instance, the primer coating may be applied to the film substrate between the two stages (longitudinal and transverse) of a biaxial stretching operation. Thus, the film substrate may be stretched firstly in the longitudinal direction over a series of rotating rollers, coated with the primer coating composition, and then stretched transversely in a stenter oven, and preferably then heat-set. Alternatively, however, the primer coating composition is applied before any stretching of the cast film.

Prior to deposition of the primer coating composition onto the substrate, the exposed surface thereof may, if desired, be subjected to a chemical or physical surface-modifying treatment to improve the bond between that surface and a subsequently applied coating or radiation-curable ink.

Physical surface-modifying treatments include flame treatment, ion bombardment, electron beam treatment, ultra-violet light treatment and corona discharge. A preferred treatment, because of its simplicity and effectiveness is to subject the exposed surface of the substrate to a high voltage electrical stress accompanied by corona discharge. Corona discharge may be effected in air at atmospheric pressure with conventional equipment using a high frequency, high voltage generator, preferably having a power output of from 1 to 20 kw at

a potential of 1 to 100 kv. Discharge is conventionally accomplished by passing the film over a dielectric support roller at the discharge station at a linear speed preferably of 1.0 to 500 m per minute. The discharge electrodes may be positioned 0.1 to 10.0 mm from the moving film surface.

Alternatively, or in addition to a physical surface-modifying treatment, the primer coating composition may be applied in combination with a surfactant which is chemically unreactive with the primer. This surfactant promotes wetting of the substrate with the aqueous coating solution in order to improve adhesion, and may be selected from anionic and nonionic surfactants such as polyoxyethylene alkylphenyl ether, polyoxyethylene-fatty acid ester, sorbitan fatty acid ester, glycerine fatty acid ester, fatty acid metal soap, alkyl sulfate, alkyl sulfonate and alkyl sulfosuccinate. The surfactant may be used in a proportion of 0 to 10% by weight, preferably 0 to 8% by weight, more preferably 0 to 4% by weight based on the composition forming the primer coating layer.

The primer coating composition may be applied to the polyester film substrate as an aqueous solution, an aqueous dispersion or emulsion by any suitable conventional coating technique such a gravure roll coating, reverse roll coating, dip coating, bead coating, slot coating or electrostatic spray coating. Preferably, the application of the primer coating is effected to provide a dry coat weight within the range 0.1 to 10 mg/dm$^2$, preferably 0.2 to 5 mg/dm$^2$, and typically within the range 0.2 to 4 mg/dm$^2$.

In order to provide effective adhesion, the primer coating layer preferably has a thickness in the range of about 0.01 to 1.0 μm, preferably in the range of about 0.02 to about 0.25 μm. If the primer coating is not thick enough, the adhesive force will be insufficient, while if coating is too thick, the haze and/or handleability of the film may be adversely affected.

The primed film may be subjected to a further physical surface-modifying treatment to improve the bond between that surface and a subsequently applied coating.

The acrylic resin of the secondary layer preferably comprises at least one monomer derived from an ester of acrylic acid and/or an ester of methacrylic acid, and/or derivatives thereof.

In a preferred embodiment of the invention, the acrylic resin comprises greater than 50 mole %, more preferably from 60 to 100 mole %, especially from 70 to 100 mole %, and particularly from 80 to 100 mole % of at least one monomer derived from an ester of acrylic acid and/or an ester of methacrylic acid, and/or derivatives thereof.

A preferred acrylic resin for use in the present invention comprises an alkyl ester of acrylic and/or methacrylic acid where the alkyl group contains up to ten carbon atoms such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, terbutyl, hexyl, 2-ethylhexyl, heptyl, and n-octyl. Preferably, the alkyl group contains 1 to 8 carbon atoms, more preferably 1 to 4 carbon atoms. Polymers derived from an alkyl acrylate, for example ethyl acrylate and butyl acrylate, are preferred, preferably together with an alkyl methacrylate. Polymers comprising ethyl acrylate and an alkyl methacrylate, preferably methyl methacrylate, are particularly preferred. The acrylate monomer is preferably present in a proportion in the range 30 to 65 mole %, and the methacrylate monomer is preferably present in a proportion in the range of 20 to 60 mole %.

Other monomers which are suitable for use in the preparation of the acrylic resin of the secondary layer, which are preferably copolymerised as optional additional monomers together with esters of acrylic acid and/or methacrylic acid, and/or derivatives thereof, include acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile, halo-substituted acrylonitrile, halo-substituted methacrylonitrile, acrylamide, methacrylamide, N-methylol acrylamide, N-ethanol acrylamide, N-propanol acrylamide, N-methacrylamide, N-ethanol methacrylamide, N-methyl acrylamide, N-tertiary butyl acrylamide, hydroxyethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, dimethylamino ethyl methacrylate, itaconic acid, itaconic anhdyride and half esters of itaconic acid.

Other optional monomers of the acrylic resin adherent layer polymer include, but are not limited to, vinyl esters such as vinyl acetate, vinyl chloracetate and vinyl benzoate, vinyl pyridine, vinyl chloride, vinylidene chloride, maleic acid, maleic anhydride, styrene and derivatives of styrene such as chloro styrene, hydroxy styrene and alkylated styrenes, wherein the alkyl group contains from one to ten carbon atoms.

A preferred acrylic resin is a copolymer of at least one alkyl acrylate, at least one alkyl methacrylate and up to 20% by weight of at least one unsaturated carboxylic acid such as acrylic, methacrylic and maleic acid, particularly acrylic and/or methacrylic acid. A particularly preferred acrylic resin is a copolymer of a $C_{1-4}$ alkyl acrylate (preferably ethyl acrylate), a $C_{1-4}$ alkyl methacrylate (preferably methyl methacrylate), and acrylic and/or methacrylic acid (preferably methacrylic acid). In this preferred embodiment, the copolymer preferably comprises from 40 to 80 weight %, particularly from 50 to 70 weight %, of monomer residues derived from the $C_{1-4}$ alkyl methacrylate component, from 15 to 55 weight %, particularly from 25 to 45 weight %, of monomer residues derived from the $C_{1-4}$ alkyl acrylate component, and from 2 to 6 weight %, particularly from 3 to 5 weight %, of monomer residues derived from the acrylic and/or methacrylic acid component, all percentages being based on the total weight of the copolymer.

Preferably the glass transition temperature of the acrylic resin is in the range of from 20 to 120°C, preferably in the range of from 30 to 100°C, more preferably in the range of from 40 to 80°C and particularly in the range of from 40 to 60°C.

The weight average molecular weight of the acrylic resin of the secondary layer can vary over a wide range but is preferably within the range 10,000 to 10,000,000, and more preferably within the range 20,000 to 200,000, more preferably within the range 25,000 to 100,000, and particularly within the range 30,000 to 60,000.

The acrylic resin preferably comprises at least 50% by weight, more preferably at least 75%, more preferably at least 90%, and more preferably greater than 95% by weight relative to the total weight of the secondary layer. In one embodiment, there are no ethylenically unsaturated compounds (for instance ester derivatives of α,β-ethylenically unsaturated acids such as acrylic, methacrylic, itaconic, citraconic, maleic or fumaric acids) present in the secondary layer additional to the acrylic resin. The acrylic resin is generally water-insoluble. The coating composition including the water-insoluble acrylic resin may nevertheless be applied to the polymeric film substrate as an aqueous dispersion.

The secondary layer may be applied to one or both surfaces of the primed polymer substrate.

The secondary coating layer may be applied in the same manner as the primer layer, and to provide a similar dry coat weight of the secondary layer, as described above. Thus, the secondary layer may be applied to an already oriented polymer film substrate, or alternatively may be applied before or during the stretching operation(s). Preferably, the secondary coating is either applied to an oriented polymer film substrate or to the film substrate between the two stages (longitudinal and transverse) of a biaxial stretching operation. More preferably, the secondary coating is applied to the polymer film substrate once all the stretching and heat-setting stages are complete. Thus, the secondary coating is preferably applied by first stretching the primed film in the longitudinal direction over a series of rotating rollers, then stretching the film transversely in a stenter oven, preferably followed by heat-setting, and then coating the primed, oriented film with the secondary coating composition. Preferably, the secondary layer is a continuous layer.

The ratio of substrate thickness to the thickness of a coating layer may vary within a wide range, although the thickness of a coating layer preferably should not be less than 0.004% nor greater than 10% of that of the substrate. In practice, the total thickness of the primer and secondary coating layers is desirably from about 0.01 μm to about 10 μm, and preferably from about 0.01 μm to about 5 μm, preferably from about 0.05 μm to about 2 μm. Generally the thickness is not more than about 1.0 μm. In a preferred embodiment, the thickness of the secondary layer is the same as, or greater than, the thickness of the primer layer. Conveniently, a secondary layer having a thickness greater than the primer layer is obtainable by applying the secondary layer after completion of the stretching and heat-setting of the primed film.

One or more of the layers of the coated film described herein may conveniently contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as dyes, pigments, voiding agents, lubricants, anti-oxidants, radical scavengers, UV absorbers, fire retardants, thermal stabilisers, anti-blocking agents, anti-static agents, catalysts for cross-linking agents, surface active agents, slip aids, optical brighteners, gloss improvers, prodegradents, viscosity modifiers and dispersion stabilisers may be incorporated in the substrate and/or coating layer(s) as appropriate. In particular the substrate and/or primer layer, may comprise a particulate filler. The filler may, for

example, be a particulate inorganic filler or an incompatible resin filler or a mixture of two or more such fillers.

By an "incompatible resin" is meant a resin which either does not melt, or which is substantially immiscible with the layer polymer, at the highest temperature encountered during extrusion and fabrication of the layer. The presence of an incompatible resin usually results in a voided layer, by which is meant that the layer comprises a cellular structure containing at least a proportion of discrete, closed cells. Suitable incompatible resins include polyamides and olefin polymers, particularly a homo- or co-polymer of a mono-alpha-olefin containing up to 6 carbon atoms in its molecule. Preferred materials include a low or high density olefin homopolymer, particularly polyethylene, polypropylene or poly-4-methylpentene-1, an olefin copolymer, particularly an ethylene-propylene copolymer, or a mixture of two or more thereof. Random, block or graft copolymers may be employed. The polymeric resin may be cross-linked.

Particulate inorganic fillers include conventional inorganic fillers, and particularly metal or metalloid oxides, such as alumina, silica (especially precipitated or diatomaceous silica and silica gels) and titania, calcined china clay and alkaline metal salts, such as the carbonates and sulphates of calcium and barium. The particulate inorganic fillers may be of the voiding or non-voiding type. Suitable particulate inorganic fillers may be homogeneous and consist essentially of a single filler material or compound, such as titanium dioxide or barium sulphate alone. Alternatively, at least a proportion of the filler may be heterogeneous, the primary filler material being associated with an additional modifying component. For example, the primary filler particle may be treated with a surface modifier, such as a pigment, soap, surfactant coupling agent or other modifier to promote or alter the degree to which the filler is compatible with the substrate layer polymer.

The inorganic filler, if used, is preferably finely-divided, and the volume distributed median particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume % to the diameter of the particles - often referred to as the "D(v,0.5)" value) thereof is preferably in the range from 0.01 to 5 μm, more preferably 0.05 to 1.5 μm, and particularly 0.15 to 1.2 μm.

The size distribution of inorganic filler particles is also an important parameter, for example the presence of excessively large particles can result in the film exhibiting unsightly 'speckle', i.e. where the presence of individual filler particles in the film can be discerned with the naked eye. It is preferred that none of the inorganic filler particles should have an actual particle size exceeding 30 µm. Particles exceeding such a size may be removed by sieving processes which are known in the art. However, sieving operations are not always totally successful in eliminating all particles greater than a chosen size. In practice, therefore, the size of 99.9% by number of the inorganic filler particles should not exceed 30 µm, preferably should not exceed 20 µm, and more preferably should not exceed 15 µm. Preferably at least 90%, more preferably at least 95% by volume of the inorganic filler particles are within the range of the volume distributed median particle diameter ± 0.8 µm, and particularly ± 0.5 µm.

Particle size of the filler particles may be measured by electron microscope, coulter counter, sedimentation analysis and static or dynamic light scattering. Techniques based on laser light diffraction are preferred. The median particle size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile.

If employed in a coating layer, the filler particles, such as Aerosil™ OX50 or Seahostar™ KEP30 or KEP50, may be present in an amount of from about 0 to about 5%, and more preferably 0.1 to 2.5% by weight relative to the weight of the polymer of the coating layer.

Either the primer layer or the secondary layer or both may contain filler particles. In a preferred embodiment, the substrate layer is unfilled.

The components of the composition of a layer may be mixed together in a conventional manner. For example, by mixing with the monomeric reactants from which the layer polymer is derived, or the components may be mixed with the polymer by tumble or dry blending or by compounding in an extruder, followed by cooling and, usually, comminution into granules or chips. Masterbatching technology may also be employed.

In one embodiment, the substrate layer is optically clear, preferably having a % of scattered visible light (haze) of <6%, more preferably <3.5 % and particularly <2%, measured according to the standard ASTM D 1003. In this embodiment, the substrate layer is unfilled or filler is typically present in only small amounts, generally not exceeding 0.5% and preferably less than 0.2% by weight of the substrate polymer.

In an alternative embodiment of the invention, the substrate layer is opaque and highly filled, preferably exhibiting a Transmission Optical Density (TOD) (Sakura Densitometer; type PDA 65; transmission mode) in the range from 0.1 to 2.0, more preferably 0.2 to 1.5, more preferably from 0.25 to 1.25, more preferably from 0.35 to 0.75 and particularly 0.45 to 0.65. The substrate layer is conveniently rendered opaque by incorporation into the polyester blend of an effective amount of an opacifying agent. Suitable opacifying agents include an incompatible resin filler, a particulate inorganic filler or a mixture of two or more such fillers, as hereinbefore described. The amount of filler present in an opaque substrate layer is preferably in the range from 1% to 30%, more preferably 3% to 20%, particularly 4% to 15%, and especially 5% to 10% by weight, based on the weight of the substrate layer polymer.

The incorporation of a particulate material into a coating layer can assist in the handling of the film, for instance to improve windability and minimise or prevent "blocking". In the embodiments described herein wherein the film is only primed and coated on one side of the substrate, the reverse side of the substrate may optionally be coated with a "slip coating" to improve the handleability of the film. Suitable slip coatings may comprise potassium silicate, such as that disclosed in, for example, US Patent Nos. 5925428 and 5882798, the disclosures of which is incorporated herein by reference. Alternatively, a slip coating may comprise a discontinuous layer of an acrylic and/or methacrylic polymeric resin optionally further comprising a cross-linking agent, as disclosed in, for example, EP-A-0408197, the disclosure of which is incorporated herein by reference.

Alternatively, the reverse side of the substrate may optionally be coated with a protective coating, or a "hard-coat", in order to improve the durability and/or scratch-resistance of the film. Suitable hard-coatings include radiation-cured acrylics (which are generally highly cross-linked), such as disclosed in US-6,265,133 and US-5,998,013; radiation-cured

urethane-acrylics, such as disclosed in US-6,110,988; hybrid organic/inorganic coatings, such as disclosed in US-6,072,018 and US-5,665,814; electron beam-cured compositions, such as disclosed in US-6,017,974; and thermally-cured compositions, such as methylolmelamine compositions (for instance as disclosed in US-4,442,177), organopolysiloxanes compositions (for instance as disclosed in US-3,707,397), polyester-melamine or acrylic-melamine compositions (for instance as disclosed in US-3,843,390), and allyl resins (for instance as disclosed in US- 2,332,461). Other hard coatings are disclosed in US-3,968,305, US-3,968,309, US-4,198,465, US- 4,319,811. The disclosures of these documents are incorporated herein by reference.

In one embodiment, the reverse side of the substrate is first coated with the two-layer coating described herein prior to application of a hard-coat protective layer, particularly a radiation-cured acrylic hard-coat protective layer, on the reverse side of the substrate, particularly wherein the primer coating layer comprises an aqueous polyester as described herein. Such a primer layer has good solvent-resistance to the solvents typically used in the application of a hard-coat, thereby improving adhesion of the hard-coat to the substrate. The secondary layer on the reverse side of the substrate may be cross-linked or uncross-linked, but is preferably uncross-linked or has a low degree of cross-linking in order to provide a symmetric film. The primer layers and secondary layers on opposite sides of the substrate may each be the same or different, but are preferably the same to provide a symmetrically coated substrate. In an alternative embodiment, the reverse side of the substrate onto which a hard-coat is applied is coated only with the primer layer described herein, preferably a primer layer comprising an aqueous polyester as described herein. Preferably, the substrate is coated with a primer layer and a secondary layer on both sides thereof.

The provision of a printing film which has a symmetric cross-section, i.e. a film comprising a substrate having the same coating composition on both sides thereof, provides particular advantages in that the manufacturing process thereof becomes more efficient and cost-effective. The symmetric film also provides advantages of ease of use and handling in applications wherein a subsequent coating is applied onto only one side of the film, such as a subsequently applied hard coating, or in applications wherein opposite sides of the film are coated with different compositions.

The printed films obtainable using the invention may be used in a variety of applications, such as the graphics layer in membrane touch switches (including panels on electronic equipment such as microwave ovens etc). A membrane touch switch is usually constructed from three, four or more layers of polymeric film. A typical switch will have a graphics layer, beneath which are two membranes or circuitry layers, each of which is screen-printed with conducting ink circuitry, separated by a spacer film with die cut holes. Contact between the circuits is achieved by finger pressure over the die cut holes. The graphics layer is usually reverse printed using a wide variety of radiation-cured inks and lacquers, as well as thermally-cured solvent inks and lacquers. The circuitry layers may also be printed using radiation- and/or thermally-cured dielectric and conductive inks. The graphics layer is generally transparent so the image can be viewed when reverse printed, while the circuit layers are usually hazy. The primed films described herein are particularly suitable for use as a graphics layer in a membrane touch switch, but may also be used as the circuitry layer therein. The coated film of the present invention may also be of use in other applications requiring radiation-resistant adhesion, particularly UV-resistant adhesion.

The following test methods may be used to determine certain properties of the polymeric film:

(i) Wide angle haze is measured using a Hazegard System XL-211, according to ASTM D 1003-61.

(ii) Adhesion of the coated film to UV–curable inks was measured using the following inks:

Dense Black 071-009 (Sericol Inc.)

Opaque White MSK-1046 (NorCote International Inc.)

The UV curable inks were applied to the coated film using a 390 mesh screen printing rig. This allowed a uniform amount of coating to be applied to the film in a reproducible manner. The inks were cured using a UV curer (at 46 feet/min using a Type H bulb at 263 mJ/cm$^2$). Separate samples of the coated film were passed through the UV curer 9 times before the inks were applied. The ink curing stage was thus the tenth curing iteration. A control sample was also tested without the initial 9 UV passes. The inked surfaces were then scored with a cross hatch tool. The tool consists of six blades with blade protrusion approximately 0.006 inch. The

film is scored four times at a 45 degree angle to the machine direction of the film. A second set of four score marks is made at right angles to the first. This gives four areas of 25 squares. To the scored area, a length of adhesive tape (3M 600 Tape) approximately 75 mm long is applied and smoothed out to exclude any trapped air. The tape is then pulled away, keeping the tape at an acute angle to the film surface. The number of squares of ink that are removed by the tape give a percentage failure for ink adhesion.

(iii) Intrinsic Viscosity is measured on a 1% (weight/volume) solution of the polymer in *o*-chlorophenol at a temperature of 25°C in accordance with standard methods.

The invention is further illustrated by the following examples. It will be appreciated that the examples are for illustrative purposes only and are not intended to limit the invention as described above. Modification of detail may be made without departing from the scope of the invention.

## EXAMPLES

### Example 1

A molten web of polyethylene terephthalate (PET) was extruded in a conventional manner from a slot die on to the polished surface of a cooled rotating drum upon which the web was quenched to below the glass transition temperature of the polymer to provide an amorphous film. The film was passed through a corona discharge treater at about 1.8 to 2.0 kW (about 1.3 J/cm$^2$) each side, and then coated on both sides with a primer coating composition comprising the following ingredients:

1. A copolyester comprising terephthalic acid (97 mol %), isophthalic acid (1 mol %), sodium 5-sulphoisophthalate (2 mol %), ethylene glycol (60 mol%), and addition product of 1 molar bisphenol a with 4 molar ethylene oxide (40 mol %) (IV = 0.58); in the form of a 21% w/w aq. dispersion : 5.6 litres.

   The dispersion may be prepared by heating the copolyester in a mixture of water and dioxan containing a surfactant, and removing the dioxan by distillation. Alternatively, the surfactant is added after removal of the dioxan. The surfactant was nonylphenylethoxylate (at approximately 15% by weight (as solids)) although other

surfactants (including alkyl ethoxylates, and particularly alkyl ethoxylate propylates (alkyl-EOPOs)) may also be used.

2. Distilled Water : 19.3 litres

The coated film was dried in a conventional web drier and then reheated and drawn about 3.5 times its original length in the longitudinal direction at a temperature of about 80°C. The monoaxially oriented PET film was then passed into a stenter oven, where the film was stretched in the sideways direction to approximately 3.5 times its original dimensions. The coated biaxially stretched film was heat-set at a temperature of about 215°C by conventional means and then passed through a corona discharge treater at about 2.5 to 3.0 kW (approximately 0.15 J/cm$^2$).

The biaxially stretched film was then coated on both sides with a secondary layer of an acrylic resin composition:

1. Acrysol WS-50 (38% w/w aq. dispersion supplied by Rohm & Haas) : 6.5 litres;
2. Seahostar KEP30 (powder supplied by Nippon Shokubai; incorporated into the coating layer to improve the slip properties of the film; used as a 15% w/w dispersion in water with 0.035% dodecylsulphate dispersion aid) : 150mls; and
3. Distilled Water : 118.5 litres.

The final film thickness was 175 µm. The dry coat weight of the first coating layer was approximately 0.50mgdm$^{-2}$, and the thickness was approximately 0.050 µm. The dry coat weight of the secondary coating layer was approximately 1.00mgdm$^{-2}$ and the thickness was approximately 0.06 µm.

**Example 2**

The procedure in example 1 was repeated except that the secondary coating layer had the following composition:

1. Neocryl BT36 (20% dispersion of a methylmethacyrlate/ethylacrylate/methacrylic acid resin; supplied by Avecia Neoresins) : 25 litres;
2. Distilled water : 225 litres;
3. Emulgator K30 surfactant (10% in water) : 250 ml; and

4. Seahostar KEP30 (powder supplied by Nippon Shokubai; incorporated into the coating layer to improve the slip properties of the film; used as a 15% w/w dispersion in water with 0.035% dodecylsulphate dispersion aid) : 300mls.

**Example 3**

This is a comparative example not according to the invention. The secondary coating layer composition of example 1 (prepared at 4% solids) was applied off-line to the biaxially stretched, heat-set and corona-treated substrate, without application of the primer layer. The secondary coating was applied using a No.0 Meyer bar and dried at 120°C for 90 seconds. The dry coat weight was about 1.40 mgdm$^{-2}$.

**Example 4**

This is a comparative example not according to the invention. The procedure of Example 3 was repeated using a crosslinking agent (modified melamine formaldehyde resin (Cymel® 301; Cytec Industries (Cyanamid))) at about 12% of the resin solids.

**Example 5**

The procedure of example 1 was repeated except that the primer coating composition had the following composition:

1. An aqueous copolyester comprising naphthalene dicarboxylic acid (60 mol %), isophthalic acid (36 mol %), sodium 5-sulphoisophthalic acid (4 mol %), ethylene glcyol (60 mol %), and addition product of 1 mole bisphenol A with 2 moles propylene oxide (40 mol %). (14% w/w aq. dispersion) : 4965 grams. (The dispersion may be made as described for Example 1. In this case, the surfactant used was alkyl-EOPO (5.3% as solid.)
2. Aerosil OX-50 (silica powder supplied by Degussa-Huls AG; incorporated into the primer coating to improve the slip properties of the film; used as a 10% w/w dispersion in water) : 375 ml;
3. Emulgator K30 (10% in water) : 40 ml;
4. Distilled water : 9.6 litres

**Example 6**

The procedure of example 1 was repeated except that the film was not passed through a corona discharge treater and the primer coating composition had the following composition:

1. Gerol PS20 ® (17.8% w/w aq. dispersion of an ethylene glycol/diethylene glycol/terephthalic acid/isophthalic acid/5-SIPA resin; supplied by Rhone Poulenc): 9.45kg
2. Cymel ®301 (100% melamine formaldehyde resin): 471g
3. Ammonium sulphate: 23.5g
4. Standapol™ A (30% ammonium lauryl sulphate; supplied by Henkel): 381g
5. Aerosol™ OT-75 (75% sodium dioctyl sulphosuccinate in ethanol/water; supplied by American Cyanamid): 69.9g
6. Dimethylaminoethanol: 145g
7. Isopropanol: 1.045kg
8. Deionised water: 79.3kg
9. Aerosil™ OX50 (silica powder supplied by Degussa-Huls AG; incorporated into the primer coating to improve the slip properties of the film; used as a 13% dispersion in water): 3.6kg

The secondary coating layer had the following composition:

1. Rhoplex™ AC73T ( 46.5% copolymer of ethyl acrylate/methyl methacrylate; supplied by Rohm & Haas): 1.7 kg
2. Deionised water: 14.2 kg

The films of the above Examples were analysed using the adhesion test described herein and the results are given in Table 1.

**Table 1**

| Example | Percentage ink removed | | | |
|---|---|---|---|---|
| | Black 1 pass | Black 10 passes | White 1 pass | White 10 passes |
| 1 | 0 | 10 | 0 | 10 |
| 2 | 0 | 0 | 10 | 0 |
| 3 | 100 | 100 | 90 | 100 |
| 4 | 30 | 90 | 10 | 90 |
| 5 | 0 | 0 | 0 | 5 |
| 6 | Not tested | 0 | Not tested | 0 |

## CLAIMS

1. Use of a primer layer and a secondary layer as a coating on a polymeric substrate, wherein the primer layer is in contact with the substrate layer and the secondary coating layer is in contact with the primer layer, wherein said secondary layer comprises an acrylic resin, and wherein said secondary layer is not cross-linked or comprises less than 5% by weight of a cross-linking agent based on the weight of the acrylic resin in the secondary coating composition, for the purpose of improving adhesion of radiation-curable ink to said substrate in a printing process comprising a plurality of radiation-curing steps.

2. A method of improving the adhesion of radiation-curable ink to a polymeric substrate in a printing process comprising a plurality of radiation-curing steps, said method comprising the application of a primer layer to a surface of said substrate and said method further comprising the application of a secondary layer comprising an acrylic resin to a primed surface of said primed substrate, and wherein said secondary layer is not cross-linked or comprises less than 5% by weight of a cross-linking agent based on the weight of the acrylic resin in the secondary coating composition.

3. Use or method according to claim 1 or 2 wherein said radiation-curable ink comprises an acrylate resin.

4. Use or method according to claim 1 or 2 wherein said radiation-curable ink comprises one or more resin(s) selected from the group consisting of acrylic resins, urethane-acrylate resins, epoxy-acrylate resins and polyester acrylate resins.

5. Use or method according to any preceding claim wherein said radiation-curable ink forms at least part of an image or design generated using a plurality of radiation-cured inks and a plurality of radiation-curing steps.

6. Use or method according to claim 5 wherein said image is generated using from 2 to 10 radiation curing steps.

7. Use or method according to any preceding claim wherein said radiation is UV radiation.

8. A use or method according to any of claims 1 to 7 wherein said secondary layer comprises less than 2% by weight of a cross-linking agent, based on the weight of the acrylic resin in the secondary coating composition.

9. A use or method according to any of claims 1 to 7 wherein said secondary layer comprises less than 1% by weight of a cross-linking agent, based on the weight of the acrylic resin in the secondary coating composition.

10. A polymeric film comprising a polymeric substrate having on at least one surface thereof a coating comprising a primer layer and a secondary layer, wherein the primer layer is in contact with the substrate layer and the secondary coating layer is in contact with the primer layer, wherein said secondary layer comprises an acrylic resin, and wherein the secondary layer is not cross-linked or comprises less than 1% by weight of a cross-linking agent.

11. A use, method or film according to any preceding claim wherein said secondary layer comprises less than 0.5% by weight of a cross-linking agent based on the weight of the acrylic resin in the secondary coating composition.

12. A use, method or film according to any preceding claim wherein the secondary layer is not cross-linked.

13. A use, method or film according to any preceding claim wherein the polymer substrate comprises a polyester.

14. A use, method or film according to any preceding claim wherein the polymer substrate comprises poly(ethylene terephthalate).

15. A use, method or film according to claim 13 wherein said primer layer exhibits good adhesion to the polyester substrate and to the acrylic resin of the secondary layer.

16. A use, method or film according to any preceding claim wherein said primer layer comprise an aqueous polyester.

17. A use, method or film according to claim 16 wherein said aqueous polyester comprises one or more polycarboxylic acid components selected from terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid and 5-sodiumsulfoisophthalic acid (5-SIPA).

18. A use, method or film according to claim 16 or 17 wherein said aqueous polyester comprises one or more polyhydroxy components selected from ethylene glycol and addition product of bisphenol A with alkylene oxide.

19. A use, method or film according to any of claims 16 to 18 wherein the polycarboxylic acid component of the aqueous polyester comprises terephthalic acid at 40-95 mol% and 5-sodiumsulphoisophthalic acid (5-SIPA) at 0.5-5 mol% of the total acid component; and the polyhydroxy component of the aqueous polyester comprises ethylene glycol and an etherglycol, wherein the etherglycol comprises 5-70 mol%of the total glycol component, and wherein the etherglycol has formula (I),

$$H(OC_nH_{2n})_m\text{-}O\text{-}A\text{-}O\text{-}(C_nH_{2n}O)_lH \qquad (I)$$

wherein

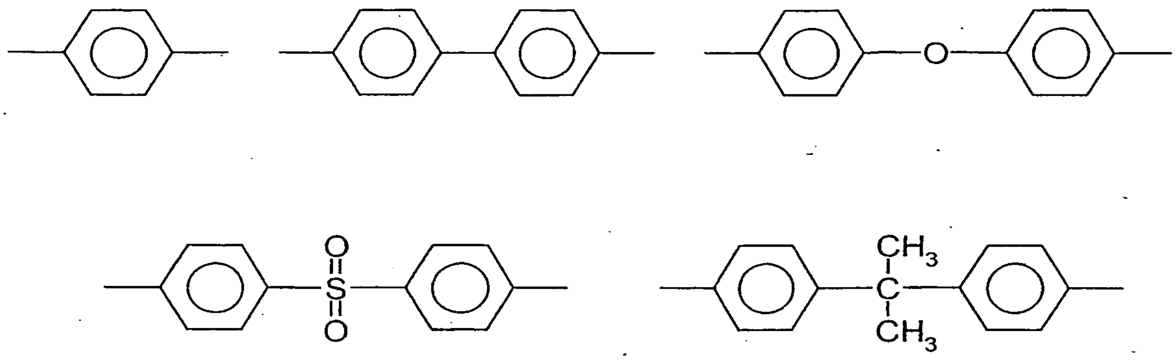
A is a bivalent aromatic hydrocarbon having 6 - 20 carbon atoms;

n is an integer 2 – 4; and

l and m, which can be the same or different, are 0, 1 or higher wherein $2 \leq \overline{(m+l)} \leq 10$.

20. A use, method or film according to claim 19 wherein the aqueous polyester further comprises isophthalic acid at a level of no more than 50 mol % of the total acid component of the aqueous polyester.

21. A use, method or film according to claim 19 or 20 wherein the group A in the etherglycol of formula (I) is selected from:



22. A use, method or film according to claim 16 wherein said aqueous polyester is selected from the group consisting of:

(a) a copolyester comprising terephthalic acid (90 mol %), isophthalic acid (6 mol %), potassium 5-sulfoisophthalate (4 mol %), ethylene glycol (95 mol %) and neopentyl glycol (5 mol %) (Tg=68°C);

(b) a copolyester comprising 2,6-naphthalenedicarboxylic acid (50 mol %), terephthalic acid (46 mol %), sodium 5-sulfoisophthalate (4 mol %), ethylene glycol (70 mol %), and addition product of bisphenol A with ethylene oxide (30 mol %) (Tg=80°C);

(c) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (15 mol %), ethylene glycol (57 mol %), 1,4-butanediol (40 mol %), diethylene glycol (2 mol %), and polyethylene glycol (1 mol %) (Tg=47°C);

(d) a copolyester comprising terephthalic acid (70 mol %), isophthalic acid (28 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (30 mol %) (Tg=30°C);

(e) a copolyester comprising 2,6-naphthalenedicarboxylic acid (71 mol %), isophthalic acid (15 mol %), sodium 5-sulfoisophthalate (14 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 2 molar ethylene oxide (30 mol %) (Tg=90°C);

(f) a copolyester comprising terephthalic acid (50 mol %), isophthalic acid (48 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (50 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (50 mol %) (IV = 0.55);

(g) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (13 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (50 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (50 mol %) (IV = 0.61);

(h) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (13 mol %), sodium 5-sulfoisophthalate (2 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (30 mol %) (IV = 0.65); and

(i) a copolyester comprising terephthalic acid (85 mol %), isophthalic acid (11 mol %), sodium 5-sulfoisophthalate (4 mol %), ethylene glycol (70 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (30 mol %) (IV = 0.58).

(j) a copolyester comprising terephthalic acid (97 mol %), isophthalic acid (1 mol %), sodium 5-sulphoisophthalate (2 mol %), ethylene glycol (60 mol %), and addition product of 1 molar bisphenol A with 4 molar ethylene oxide (40 mol %) (IV = 0.58);

(k) a copolyester comprising naphthalene dicarboxylic acid (60 mol%), isophthalic acid (36 mol %), sodium 5-sulphoisophthalic acid (4 mol %), ethylene glycol (60 mol %), and addition product of 1 mole bisphenol A with 2 moles propylene oxide (40 mol %).

23. A use, method or film according to any of claims 16 to 22 wherein said aqueous polyester has a glass transition point (Tg) of from 20 to 85°C.

24. A use, method or film according to any of claims 1 to 15 wherein said primer layer comprises a polyurethane resin.

25. A use, method or film according to any of claims 1 to 15 wherein said primer layer comprises an acrylic and/or methacrylic polymeric resin.

26. A use, method or film according to claim 25 wherein said primer layer comprises alkyl acrylate monomer units and alkyl methacrylate monomer units, wherein the alkyl acrylate monomer units are present in a proportion in the range of from 30 to 65 mole % and the alkyl methacrylate monomer units are present in a proportion in the range of from 20 to 60 mole %.

27. A use, method or film according to claims 25 or 26 wherein said primer layer comprises ethyl acrylate and methyl methacrylate.

28. A use, method or film according to claims 25 or 26 wherein said primer layer comprises about 35 to 60 mole % ethyl acrylate, about 30 to 55 mole % methyl methacrylate and about 2 to 20 mole % methacrylamide.

29. A use, method or film according to any of claims 16 to 28 wherein the polymer of the primer layer is present in an amount of 0.3 to 20 % by weight, based on the total weight of the primer coating layer.

30. A use, method or film according to any preceding claim wherein said acrylic resin of the secondary layer comprises at least one monomer derived from an ester of acrylic acid and/or an ester of methacrylic acid, and/or derivatives thereof.

31. A use, method or film according to claim 30 wherein said acrylic resin comprises an acrylate monomer present in a proportion in the range 30 to 65 mole %, and a methacrylate monomer present in a proportion in the range of 20 to 60 mole %.

32. A use, method or film according to claim 30 wherein said acrylic resin is a copolymer of a $C_{1-4}$ alkyl methacrylate, a $C_{1-4}$ alkyl acrylate and acrylic and/or methacrylic acid with a glass transition temperature in the range 30 to 100 °C.

33. A use, method or film according to any preceding claim wherein the primer layer and/or the secondary layer comprises a particulate material, said particulate material being amorphous silica having a mean diameter of 0.1 to 5.0 μm.

34. A use, method or film according to any preceding claim wherein the film is biaxially oriented.

# INTERNATIONAL SEARCH REPORT

Interr l Application No
PCT/GB 03/00976

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 C08J7/04 B41M5/00 C09D133/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO 97 27064 A (UCB SA ;MARSHALL COLIN (GB); POWER GARY (GB); SERVANTE ALASTAIR HU) 31 July 1997 (1997-07-31)<br>claims 1-4,6,7,13<br>page 3, line 1 - line 15<br>page 3, line 30 -page 4, line 2<br>page 5, line 5 - line 17<br>page 8, line 14 -page 9, line 3<br>--- | 1,3-5,8, 10-12, 15,33,34 |
| X | GB 971 342 A (ILFORD LTD)<br>30 September 1964 (1964-09-30) | 10-18,30 |
| Y | claims 1,12<br>page 2, line 97 - line 108<br>page 3, line 72 - line 75<br>example 8(a)<br>--- | 10-22 |
| | -/-- | |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 5 June 2003 | 17/06/2003 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Hallemeesch, A |

Form PCT/ISA/210 (second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

Interna Application No
PCT/GB 03/00976

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | PATENT ABSTRACTS OF JAPAN<br>vol. 014, no. 126 (C-0699),<br>9 March 1990 (1990-03-09)<br>& JP 02 003419 A (TEIJIN LTD),<br>9 January 1990 (1990-01-09)<br>abstract<br>--- | 10-22 |
| A | US 5 910 370 A (KATSURA NAOMI ET AL)<br>8 June 1999 (1999-06-08)<br>cited in the application<br>claims 1-3<br>--- | 10,24 |
| A | US 4 066 820 A (KELLY ROGER SIDNEY ARTHUR ET AL) 3 January 1978 (1978-01-03)<br>claims 6-8<br>--- | 10,25-29 |
| A | DE 36 27 973 A (RENKER GMBH & CO KG)<br>25 February 1988 (1988-02-25)<br>claims 1-3<br>----- | 1,10 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Intern Application No
PCT/GB 03/00976

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 9727064 A | 31-07-1997 | AT 185745 T | 15-11-1999 |
| | | AU 725708 B2 | 19-10-2000 |
| | | AU 1433497 A | 20-08-1997 |
| | | WO 9727064 A1 | 31-07-1997 |
| | | BR 9707198 A | 28-12-1999 |
| | | CN 1209777 A ,B | 03-03-1999 |
| | | DE 69700652 D1 | 25-11-1999 |
| | | DE 69700652 T2 | 08-06-2000 |
| | | EP 0876259 A1 | 11-11-1998 |
| | | ES 2140955 T3 | 01-03-2000 |
| | | HR 970037 A1 | 30-04-1998 |
| | | JP 2000513663 T | 17-10-2000 |
| | | PT 876259 T | 28-04-2000 |
| | | RU 2170178 C2 | 10-07-2001 |
| | | TW 419420 B | 21-01-2001 |
| | | US 2002098340 A1 | 25-07-2002 |
| | | ZA 9700523 A | 30-07-1997 |
| GB 971342 A | 30-09-1964 | GB 954453 A | 08-04-1964 |
| | | BE 626241 A | |
| JP 02003419 A | 09-01-1990 | JP 2593188 B2 | 26-03-1997 |
| US 5910370 A | 08-06-1999 | AU 7183996 A | 29-05-1997 |
| | | CA 2190542 A1 | 22-05-1997 |
| | | EP 0776928 A1 | 04-06-1997 |
| | | JP 9174764 A | 08-07-1997 |
| | | US 5667889 A | 16-09-1997 |
| US 4066820 A | 03-01-1978 | GB 1497656 A | 12-01-1978 |
| | | GB 1497657 A | 12-01-1978 |
| | | BE 827432 A1 | 01-10-1975 |
| | | DE 2513421 A1 | 02-10-1975 |
| | | DE 2513423 A1 | 02-10-1975 |
| | | FR 2265808 A1 | 24-10-1975 |
| | | IT 1037115 B | 10-11-1979 |
| | | JP 1119479 C | 28-10-1982 |
| | | JP 50135188 A | 27-10-1975 |
| | | JP 55023150 B | 20-06-1980 |
| | | LU 72152 A1 | 19-08-1976 |
| | | NL 7503691 A ,B | 01-10-1975 |
| | | US T946007 I4 | 04-05-1976 |
| | | DE 2513422 A1 | 02-10-1975 |
| | | US T946006 I4 | 04-05-1976 |
| DE 3627973 A | 25-02-1988 | DE 3627973 A1 | 25-02-1988 |